

**PCT**

REC'D 19 APR 2001

**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

(PCT Article 36 and Rule 70)

14


Applicant's or agent's file reference <b>P7259WO DAA</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/GB00/02827</b>	International filing date (day/month/year) <b>21/07/2000</b>	Priority date (day/month/year) <b>30/07/1999</b>
International Patent Classification (IPC) or national classification and IPC <b>C02F1/44</b>		
Applicant <b>MEMBRANE EXTRACTION TECHNOLOGY LIMITED et al.</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.  
  
☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand <b>23/01/2001</b>	Date of completion of this report <b>11.04.2001</b>
Name and mailing address of the international preliminary examining authority:   <b>European Patent Office</b> <b>D-80298 Munich</b> <b>Tel. +49 89 2399 - 0 Tx: 523656 epmu d</b> <b>Fax: +49 89 2399 - 4465</b>	Authorized officer  <b>Assogna, R</b>  <b>Telephone No. +49 89 2399 8354</b>



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB00/02827

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-19 as originally filed

**Claims, No.:**

1-33 as originally filed

**Drawings, sheets:**

1/6-6/6 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB00/02827

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application.

☒ claims Nos. 33.

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 33 are so unclear that no meaningful opinion could be formed (*specify*):  
**see separate sheet**

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos. .

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)

Yes: Claims 1-32

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/02827

	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-32
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-32
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

## VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

**see separate sheet**

## VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:  
**see separate sheet**

## VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**Re Item III**

**Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

Since claim 33 does not contain any technical feature, no opinion can be given with regard to novelty, inventive step and industrial applicability of this claim.

**Re Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

The subject-matter of claim 1 is novel since in none of the cited documents is disclosed that the aromatic amines are transferred to the acidic stripping solution, that the volume and the pH of stripping solution are regulated and adjusted to be above the solubility of the aromatic amines in water and above the acidic dissociation constant of the aromatic amine and the aromatic amines are separated by the acidic stripping solution.

Prior art: GB-A-2 333 473 discloses a method of transferring at least one substance across a membrane from a first fluid to a second fluid, wherein transfer of the substance from the first fluid to the second fluid occurs across the membrane; preferably the substance to be transferred from the first fluid can be an aqueous medium which contains at least one organic material.

US-A-5 585 004 discloses a method of reducing the concentration of at least one organic compound (aromatic, aniline) present in an aqueous feedstock, wherein the feedstock is supplied to one side of a tubular membrane.

By controlling the pH and volume in the acidic stripping solution a reduction of costs and increase of the membrane lifetime is achieved, particularly in respect of acidic stripping solutions.

In the present invention, the aromatic amines pass into an acidic stripping solution in which the aromatic amines undergo dissociation. The acidic stripping solution is then further processed by adjusting the pH upwards until the aromatic amines re-

associate and precipitate out of solution as liquids or solids.

**R Item VI**

**C rtain documents cited**

Certain published documents (Rule 70.10)

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
WO-A-00 00275	06.01.00	25.06.99	29.06.98

**R Item VII**

**C rtain defects in the international application**

The vague and imprecise statement (spirit of the invention) in the description on page 19 implies that the subject-matter for which protection is sought may be different to that defined by the claims, thereby resulting in lack of clarity (Article 6 PCT) when used to interpret them (see also the PCT Guidelines, III-4.3a).

**R Item VIII**

**C rtain observations on the international application**

The features of claims 9, 12 and 30 are not referred to in the description. Claims 9,12 and 30 are therefore not supported by the description as required by Article 6 PCT.

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>P7259W0 DAA</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/GB 00/ 02827</b>	International filing date (day/month/year) <b>21/07/2000</b>	(Earliest) Priority Date (day/month/year) <b>30/07/1999</b>
Applicant <b>MEMBRANE EXTRACTION TECHNOLOGY LIMITED et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

**METHOD FOR REMOVING AND RECOVERING AROMATIC AMINES BY USING A NON-POROUS MEMBRANE**

5. With regard to the **abstract**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☒ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1  
☐ None of the figures.

## Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

There is provided a process for removing and recovering one or more undissociated aromatic amines dissolved in aqueous fluid, the process comprising the steps of : (a) transferring the one or more undissociated aromatic amines from the aqueous fluid to an acidic stripping solution (3), wherein transfer of the one or more undissociated aromatic amines from the aqueous fluid to the acidic stripping solution occurs across a membrane (5); wherein the membrane is a non porous, selectively permeable membrane; (b) regulating the volume of acidic stripping solution employed relative to the volume of aqueous fluid treated so that the total aromatic amine concentration in the acidic stripping solution, comprising the sum of the dissociated and undissociated aromatic amine concentrations, is above the solubility of the aromatic amine<sup>s</sup> in water; (c) regulating the pH of the acidic stripping solution in contact with the membrane so that the membrane remains selectively permeable; (d) adjusting the pH of the aromatic amine containing acidic stripping solution to a value above the acidic dissociation constant of the aromatic amine and (e) separating the resulting aromatic amine and the acidic stripping solution.



**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C02F1/44 B01D61/36

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 333 473 A (MEMBRANE EXTRACTION TECHNOLOGY) 28 July 1999 (1999-07-28) page 6, line 6 -page 8, line 30 ---	1-32
A	US 5 585 004 A (LIVINGSTON ANDREW) 17 December 1996 (1996-12-17) cited in the application column 2, line 6 -column 4, line 54 ---	1-32
P,A	WO 00 00275 A (LIVINGSTON ANDREW GUY ;MEMBRANE EXTRACTION TECHNOLOGY (GB)) 6 January 2000 (2000-01-06) ---	
A	EP 0 485 077 A (EXXON RESEARCH ENGINEERING CO) 13 May 1992 (1992-05-13) -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* & \* document member of the same patent family

Date of the actual completion of the international search

1 December 2000

Date of mailing of the international search report

19/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Assogna, R

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 2333473	A	28-07-1999	AU	2175699 A	09-08-1999
			WO	9937390 A	29-07-1999
US 5585004	A	17-12-1996	AT	189669 T	15-02-2000
			AU	670041 B	04-07-1996
			AU	2588592 A	27-04-1993
			CA	2119383 A	01-04-1993
			DE	69230667 D	16-03-2000
			DE	69230667 T	31-08-2000
			EP	0604514 A	06-07-1994
			WO	9306045 A	01-04-1993
			JP	6510696 T	01-12-1994
WO 0000275	A	06-01-2000	GB	2338910 A	12-01-2000
			AU	4522499 A	17-01-2000
EP 0485077	A	13-05-1992	US	5234597 A	10-08-1993
			CA	2054046 A	06-05-1992
			JP	4266989 A	22-09-1992
			US	5435918 A	25-07-1995

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

ALCOCK, David  
D. Young & Co.  
21 New Fetter Lane  
London EC4A 1DA  
GRANDE BRETAGNE

MONEY	£		
ORDER			
DIARY			
REC'D	17 APR 2001		
ANNO			
CITY			
FOR			

*DS DAA*

PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing  
(day/month/year) 11.04.2001

Applicant's or agent's file reference  
P7259WO DAA

IMPORTANT NOTIFICATION

International application No.  
PCT/GB00/02827

International filing date (day/month/year)  
21/07/2000

Priority date (day/month/year)  
30/07/1999

Applicant

MEMBRANE EXTRACTION TECHNOLOGY LIMITED et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office  
D-80298 Munich  
Tel. +49 89 2399 - 0 Tx: 523656 epmu d  
Fax: +49 89 2399 - 4465

Authorized officer

Gregoire, J-P

Tel. +49 89 2399-8041



# PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>P7259WO DAA</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/GB00/02827</b>	International filing date (day/month/year) <b>21/07/2000</b>	Priority date (day/month/year) <b>30/07/1999</b>
International Patent Classification (IPC) or national classification and IPC <b>C02F1/44</b>		
Applicant <b>MEMBRANE EXTRACTION TECHNOLOGY LIMITED et al.</b>		



1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
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☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  <b>23/01/2001</b>	Date of completion of this report  <b>11.04.2001</b>
Name and mailing address of the international preliminary examining authority:   <b>European Patent Office</b> <b>D-80298 Munich</b> <b>Tel. +49 89 2399 - 0 Tx: 523656 epmu d</b> <b>Fax: +49 89 2399 - 4465</b>	Authorized officer  <b>Assogna, R</b>  Telephone No. +49 89 2399 8354 

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/02827

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

### Description, pages:

1-19 as originally filed

### Claims, No.:

1-33 as originally filed

### Drawings, sheets:

1/6-6/6 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB00/02827

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application.

☒ claims Nos. 33.

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 33 are so unclear that no meaningful opinion could be formed (*specify*):  
**see separate sheet**

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos. .

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)

Yes: Claims 1-32

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB00/02827

	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-32
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-32
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

**VI. Certain documents cited**

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

**see separate sheet**

**VII. Certain defects in the international application**

The following defects in the form or contents of the international application have been noted:  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**R Item III**

**Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

Since claim 33 does not contain any technical feature, no opinion can be given with regard to novelty, inventive step and industrial applicability of this claim.

**R Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

The subject-matter of claim 1 is novel since in none of the cited documents is disclosed that the aromatic amines are transferred to the acidic stripping solution, that the volume and the pH of stripping solution are regulated and adjusted to be above the solubility of the aromatic amines in water and above the acidic dissociation constant of the aromatic amine and the aromatic amines are separated by the acidic stripping solution.

Prior art: GB-A-2 333 473 discloses a method of transferring at least one substance across a membrane from a first fluid to a second fluid, wherein transfer of the substance from the first fluid to the second fluid occurs across the membrane; preferably the substance to be transferred from the first fluid can be an aqueous medium which contains at least one organic material.

US-A-5 585 004 discloses a method of reducing the concentration of at least one organic compound (aromatic, aniline) present in an aqueous feedstock, wherein the feedstock is supplied to one side of a tubular membrane.

By controlling the pH and volume in the acidic stripping solution a reduction of costs and increase of the membrane lifetime is achieved, particularly in respect of acidic stripping solutions.

In the present invention, the aromatic amines pass into an acidic stripping solution in which the aromatic amines undergo dissociation. The acidic stripping solution is then further processed by adjusting the pH upwards until the aromatic amines re-



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/GB00/02827

associate and precipitate out of solution as liquids or solids.

**R Item VI**

**Certain documents cited**

Certain published documents (Rule 70.10)

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
WO-A-00 00275	06.01.00	25.06.99	29.06.98

**R Item VII**

**Certain defects in the international application**

The vague and imprecise statement (spirit of the invention) in the description on page 19 implies that the subject-matter for which protection is sought may be different to that defined by the claims, thereby resulting in lack of clarity (Article 6 PCT) when used to interpret them (see also the PCT Guidelines, III-4.3a).

**R Item VIII**

**Certain observations on the international application**

The features of claims 9, 12 and 30 are not referred to in the description. Claims 9, 12 and 30 are therefore not supported by the description as required by Article 6 PCT.

From the INTERNATIONAL SEARCHING AUTHORITY

**PCT**NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

(PCT Rule 44.1)

To:

D. Young & Co.  
Attn. ALCOCK, David  
21 New Fetter Lane  
London EC4A 1DA  
UNITED KINGDOMP/7259WO  
A.0201

DS DAA

Date of mailing  
(day/month/year)

19/12/2000

Applicant's or agent's file reference

P7259WO DAA

**FOR FURTHER ACTION**

See paragraphs 1 and 4 below

International application No.

PCT/GB 00/02827

International filing date  
(day/month/year)

21/07/2000

Applicant

MEMBRANE EXTRACTION TECHNOLOGY LIMITED et al.

- 1.
- ☒
- The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

**Filing of amendments and statement under Article 19:**

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

**When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.**Where?** Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35**For more detailed instructions,** see the notes on the accompanying sheet.

- 2.
- ☐
- The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

- 3.
- ☐
- With regard to the protest**
- against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

- 4.
- Further action(s):**
- The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority

European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Véronique Baillou

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

## INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

### What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

### What documents must/may accompany the amendments?

#### Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

**"Statement under article 19(1)" (Rule 46.4)**

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

**Consequence if a demand for international preliminary examination has already been filed**

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

**Consequence with regard to translation of the international application for entry into the national phase**

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>P7259W0 DAA</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/GB 00/ 02827</b>	International filing date (day/month/year) <b>21/07/2000</b>	(Earliest) Priority Date (day/month/year) <b>30/07/1999</b>
Applicant <b>MEMBRANE EXTRACTION TECHNOLOGY LIMITED et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

**METHOD FOR REMOVING AND RECOVERING AROMATIC AMINES BY USING A NON-POROUS MEMBRANE**

5. With regard to the **abstract**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☒ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1  
☐ None of the figures.

## Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

There is provided a process for removing and recovering one or more undissociated aromatic amines dissolved in aqueous fluid, the process comprising the steps of : (a) transferring the one or more undissociated aromatic amines from the aqueous fluid to an acidic stripping solution (3), wherein transfer of the one or more undissociated aromatic amines from the aqueous fluid to the acidic stripping solution occurs across a membrane (5); wherein the membrane is a non porous, selectively permeable membrane; (b) regulating the volume of acidic stripping solution employed relative to the volume of aqueous fluid treated so that the total aromatic amine concentration in the acidic stripping solution, comprising the sum of the dissociated and undissociated aromatic amine concentrations, is above the solubility of the aromatic amine in water; (c) regulating the pH of the acidic stripping solution in contact with the membrane so that the membrane remains selectively permeable; (d) adjusting the pH of the aromatic amine containing acidic stripping solution to a value above the acidic dissociation constant of the aromatic amine and (e) separating the resulting aromatic amine and the acidic stripping solution.

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C02F1/44 B01D61/36

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C02F B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 333 473 A (MEMBRANE EXTRACTION TECHNOLOGY) 28 July 1999 (1999-07-28) page 6, line 6 -page 8, line 30 ---	1-32
A	US 5 585 004 A (LIVINGSTON ANDREW) 17 December 1996 (1996-12-17) cited in the application column 2, line 6 -column 4, line 54 ---	1-32
P, A	WO 00 00275 A (LIVINGSTON ANDREW GUY ; MEMBRANE EXTRACTION TECHNOLOGY (GB)) 6 January 2000 (2000-01-06) ---	
A	EP 0 485 077 A (EXXON RESEARCH ENGINEERING CO) 13 May 1992 (1992-05-13) -----	

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* & \* document member of the same patent family

Date of the actual completion of the international search

1 December 2000

Date of mailing of the international search report

19/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Assogna, R

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 2333473	A	28-07-1999	AU	2175699 A	09-08-1999
			WO	9937390 A	29-07-1999
US 5585004	A	17-12-1996	AT	189669 T	15-02-2000
			AU	670041 B	04-07-1996
			AU	2588592 A	27-04-1993
			CA	2119383 A	01-04-1993
			DE	69230667 D	16-03-2000
			DE	69230667 T	31-08-2000
			EP	0604514 A	06-07-1994
			WO	9306045 A	01-04-1993
			JP	6510696 T	01-12-1994
WO 0000275	A	06-01-2000	GB	2338910 A	12-01-2000
			AU	4522499 A	17-01-2000
EP 0485077	A	13-05-1992	US	5234597 A	10-08-1993
			CA	2054046 A	06-05-1992
			JP	4266989 A	22-09-1992
			US	5435918 A	25-07-1995



(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
8 February 2001 (08.02.2001)

PCT

(10) International Publication Number  
**WO 01/09042 A1**

(51) International Patent Classification<sup>7</sup>: C02F 1/44,  
B01D 61/36

Limited, Dept. of Chemical Engineering, Imperial College,  
London SW7 2BY (GB).

(21) International Application Number: PCT/GB00/02827

(22) International Filing Date: 21 July 2000 (21.07.2000)

(25) Filing Language: English

(26) Publication Language: English

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9918031.7 30 July 1999 (30.07.1999) GB

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drew, Guy [GB/GB]; Membrane Extraction Technology

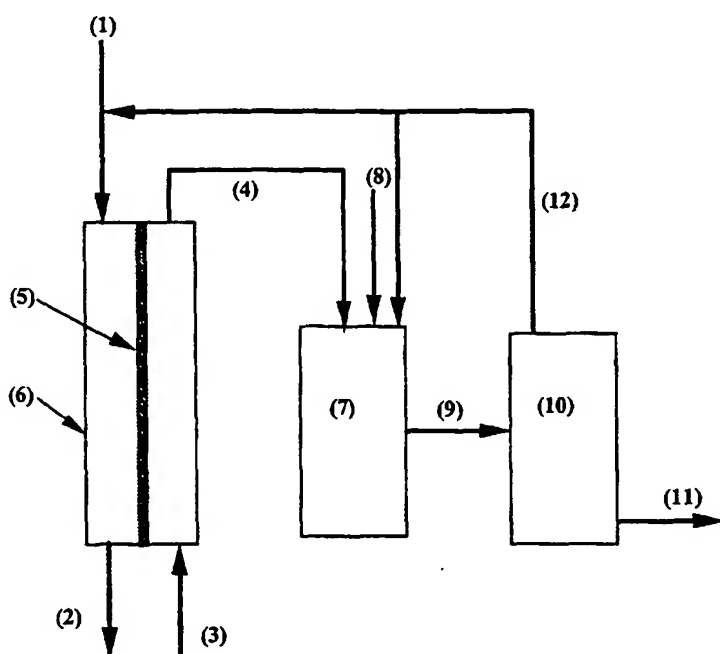
(74) Agents: ALCOCK, David et al.; D Young & Co, 21 New  
Fetter Lane, London EC4A 1DA (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
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(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,  
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHOD FOR REMOVING AND RECOVERING AROMATIC AMINES BY USING A NON-POROUS MEM-  
BRANE



Aromatic amine recovery process

(57) Abstract: There is provided a process for removing and recovering one or more undissociated aromatic amines dissolved in aqueous fluid, the process comprising the steps of: (a) transferring the one or more undissociated aromatic amines from the aqueous fluid to an acidic stripping solution (3), wherein transfer of the one or more undissociated aromatic amines from the aqueous fluid to the acidic stripping solution occurs across a membrane (5); wherein the membrane is a non porous, selectively permeable membrane; (b) regulating the volume of acidic stripping solution employed relative to the volume of aqueous fluid treated so that the total aromatic amine concentration in the acidic stripping solution, comprising the sum of the dissociated and undissociated aromatic amine concentrations, is above the solubility of the aromatic amine in water; (c) regulating the pH of the acidic stripping solution in contact with the membrane so that the membrane remains selectively permeable; (d) adjusting the pH of the aromatic amine containing acidic stripping solution to a value above the acidic dissociation constant of the aromatic amine and (e) separating the resulting aromatic amine and the acidic stripping solution.

WO 01/09042 A1

**Published:**

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## METHOD FOR REMOVING AND RECOVERING AROMATIC AMINES BY USING A NON-POROUS MEMBRANE

The present invention relates to a process for the removal and recovery of one or more aromatic amines from an aqueous fluid. In particular the process comprises transferring  
5 the aromatic amines from the aqueous fluid to an acidic stripping solution across a non porous, selectively permeable membrane, adjusting the pH of the acidic stripping solution and separating the resulting aromatic amine from the acidic stripping solution.

Many organic bases, such as aniline, toluidine, nitroaniline, enter aqueous process streams  
10 in chemical processing. These molecules are in many cases toxic. Methods for removing toxic organic molecules from aqueous process streams are well known. Some of these methods use membranes.

Membrane solvent extraction using microporous membranes to provide a phase  
15 contacting between aqueous and organic streams is well known. For example Kiani, Bhavé and Sirkar Journal of Membrane Science 20 (1984) pp 125-145 report the use of microporous membranes for immobilising solvent interfaces during solvent extraction. Tompkins, Micheals and Peretti Journal of Membrane Science 75 (1992) pp 277-292  
20 report using microporous polypropylene fibres to stabilise phase interfaces during extraction of nitrophenol from an aqueous solution into octanol. US 5,512,180 describes a process wherein polypropylene glycol MW 4000 was used to extract nitrophenol in a microporous membrane contactor.

A continuing problem with membrane supported solvent extraction with microporous  
25 membranes is the breakthrough of one phase into the other due to pressure imbalances. To overcome this problem, various improvements have been suggested such as using composite membranes comprising a thin layer of non-porous organic-permeable polymer bound to a microporous membrane to avoid phase breakthrough, for example US 4,960,520. However, in all of these processes a solvent phase containing the organic  
30 compound is produced which must then be disposed of or treated in some way.

Contacting two aqueous streams with opposite sides of a membrane to effect extraction of organic pollutants from one side to the other is also known in the art. Supported liquid membranes have been applied in this mode. For example US 5,507,949 describes a process wherein the pores of a microporous hydrophobic membrane are filled with a hydrophobic polyamphiphilic oligomeric or polymeric liquid to allow mass transport of various organics across the membranes. In this application the driving force for extraction across the supported liquid membranes may be provided by a stripping solution. The driving force produced by a stripping solution may rely upon conversion of an organic acid to its corresponding salt using a basic stripping solution, or conversion of an organic base to its corresponding salt using an acidic stripping solution. Biologically active stripping solutions may also be utilised, for example US 4,988,443 to Michaels et al. discloses a method for contacting an aqueous waste stream containing organic toxicants with a nutrient-containing aqueous stream using hollow fibre membranes with water immiscible solvent filled pores. The two streams do not mix but the organic toxicants are transferred from the waste stream across the membrane to the nutrient stream. Microorganisms growing associated with the outside of the hollow fibres utilise the nutrients and organic toxicants as growth substrates which provides the driving force for continued transport.

In further applications non-porous membranes have been employed to effect extraction of organic molecules from one aqueous stream into another. US 5,552,053 discloses solid polyamphiphilic polymer films used for keeping separate two aqueous phases, one being a waste stream and the other a stripping solution in which the organic pollutant can be concentrated by conversion into an ionised form at controlled pH.

In the above prior art, membranes are substantially rigid and are employed in shell and tube modules, in plate and frame modules, or in spiral wound modules. These modules are designed to generate good mass transfer and fluid distribution around all of the membrane surfaces.

In a few cases, tubular elastomeric non-porous homogeneous membranes for example

silicone rubber (cross linked polydimethoxysiloxane) tubes have been disclosed. The tubular elastomeric membranes provide separation by allowing specific chemical species (for example, hydrophobic organic molecules such as benzene, toluene, or their derivatives) to preferentially dissolve in the membrane and permeate across the membrane by diffusion under the influence of a chemical activity driving force. For example, US 5,585,004 to Livingston discloses a system of apparatus and method wherein a waste stream containing toxic organic compounds is fed to the inside of selectively permeable silicone rubber membrane tubes suspended in a bioreactor receptacle filled with a biologically active medium. The toxic organic compounds diffuse across the silicone rubber membrane and into the biologically active medium where they are destroyed by the microbial culture.

Further examples of the use of tubular elastomeric membranes are oxygenation of microbial systems (Cote et al, Journal of Membrane Science 1989 47 p107), and pervaporation (Raghunath and Hwang, Journal of Membrane Science 1992 65 p147). In the field of chemical analysis, silicone rubber membranes have been used to extract organics from aqueous streams prior to analysis (US 4,715,217; US 4,891,137).

The processing of organic-laden stripping solutions comprising organic acids in dissociated form in an aqueous solution is known with regard to nitrophenolic compounds recovery. For example, various processes are known in the art for disposing of stripping solutions containing nitrophenolic materials. These stripping solutions are generated as a by-product of nitration reactions. US Patent 4,597,875 discloses a process for removing the nitrophenolic materials from an alkaline stripping solution by treating the wastewater with an acid to lower its pH and convert the nitrophenolic compounds to a water insoluble solid material which is separated out of the wastewater and can be disposed of by incineration. US 4,925,565 discusses a process in which the alkaline stripping solution is treated with acid to lower its pH, following which a substantially water insoluble solvent is used to extract the nitrophenolic compounds from the wastewater at elevated temperature. The solvent is recovered by distillation and the residue containing nitrophenolics can be incinerated. In variations on US 4,925,565, the same inventors use

differential control of the pH to recover specific nitrophenolic fractions by solvent extraction (US 4,986,917) and precipitation (US 4,986,920). However, the recovery of the nitrophenolic fraction is complicated by the fact that the nitrophenols form solid precipitates upon acidification of alkaline wastewaters containing ionised nitrophenolic compounds at concentrations above the saturation concentration of non-ionised nitrophenolic compounds in water.

In the prior art utilising membranes for organics removal, the focus has been on the use of alkaline stripping solutions to remove organic acids from aqueous fluids. Many polymeric membrane materials and in particular elastomers have good resistance to alkalis. However, when it is desired to remove organic bases such as aromatic amines using acidic stripping solutions, problems can arise due to the lack of chemical resistance of many polymeric membrane materials, in particular elastomers, to mineral acids.

The present invention addresses the problems of the prior art.

In one aspect the present invention provides a process for removing and recovering one or more undissociated aromatic amines dissolved in aqueous fluid, the process comprising the steps of: (a) transferring the one or more undissociated aromatic amines from the aqueous fluid to an acidic stripping solution, wherein transfer of the one or more undissociated aromatic amines from the aqueous fluid to the acidic stripping solution occurs across a membrane: wherein the membrane is a non porous, selectively permeable membrane; (b) regulating the volume of acidic stripping solution employed relative to the volume of aqueous fluid treated so that the total aromatic amine concentration in the acidic stripping solution, comprising the sum of the dissociated and undissociated aromatic amine concentrations, is above the solubility of the aromatic amines in water; (c) regulating the pH of the acidic stripping solution in contact with the membrane so that the membrane remains selectively permeable; (d) adjusting the pH of the aromatic amine containing acidic stripping solution to a value above the acidic dissociation constant of the aromatic amine and (e) separating the resulting aromatic amine and the acidic stripping solution.

By the term "selectively permeable" it is meant a membrane which is permeable to the undissociated aromatic amine and which is impermeable to the dissociated aromatic amine.

5

It will be appreciated that the term "aromatic amine" includes any compound of the formula  $R^1NR^2R^3$  wherein  $R^1$  is or comprises an aromatic group and  $R^2$  and  $R^3$  are independently selected from H or a hydrocarbyl group, such as an alkyl or an aryl group. In this aspect an undissociated aromatic amine is a compound of the formula  $R^1NR^2R^3$  and a  
10 dissociated aromatic amine is a compound of the formula  $R^1NR^2R^3H^+$ .

Step (c) requires that the pH of the acidic stripping solution in contact with the membrane is regulated so that the membrane remains selectively permeable. By this it is meant that the pH should be regulated so that the membrane materials are not rendered unusable  
15 through attack by the acidic stripping solution.

The present inventors have found that control of the pH in the acidic stripping solution assists in the reducing of costs and in increasing the membrane lifetime, particularly in respect of acidic stripping solutions.

20

In the present invention, aromatic amines present in an aqueous fluid in undissociated form are recovered by means of membrane extraction across a membrane. The membrane contains at least one non porous, selectively permeable layer. The aromatic amines pass into an acidic stripping solution in which the aromatic amines undergo dissociation. The  
25 acidic stripping solution is then further processed by adjusting the pH upwards until the aromatic amines re-associate and precipitate out of solution as liquids or solids.

Aromatic amines will undergo a dissociation reaction when the pH of the stripping solution is below the  $pK_a = (14 - pK_b)$  of the aromatic amine, where  $pK_b$  is the basicity  
30 constant and is defined as follows (see for example "Organic Chemistry" third Edition by T.W.G.Solomons. John Wiley and Sons, pp 836-837):



$$pKb = \log_{10} \left( \frac{[RNH_3^+][OH^-]}{[RNH_2]} \right) \quad (2)$$

5

where R is an aromatic group containing organic structure.

The aromatic amine containing acidic stripping solution is subsequently neutralised to alkaline pH and the aromatic amines return to undissociated form and precipitate out of solution as organic liquids or solids. The organic liquids or solids are separated from the acidic stripping solution. The separated acidic stripping solution may contain saturation levels of undissociated aromatic amines and may be cycled back to the aqueous fluid to undergo further stripping. In the present invention the extraction and acidic stripping solution regeneration stages are integrated so that the streams leaving the process are pure organic liquid and treated aqueous waste respectively.

15

Preferably the aqueous fluid is an aqueous process stream.

Preferably the aqueous fluid is contacted with one side of the membrane and wherein the acidic stripping solution is contacted with the other side of the membrane. In a more preferred aspect prior to adjusting the pH of the aromatic amine containing acidic stripping solution, the acidic stripping solution is removed from contact with the membrane.

20

Preferably the acidic stripping solution separated in step (e) is recycled to the aqueous fluid prior to contact with the membrane. In one preferred alternative the acidic stripping solution separated in step (e) is recycled to the aromatic amine containing acidic stripping solution prior to removing the acidic stripping solution from contact with the membrane.

25

The resulting aromatic amine of step (e) may be a liquid or a solid.

30



The membrane of the present invention can be configured in accordance with any of the designs known to those skilled in the art, such as spiral wound, plate and frame, shell and tube, and derivative designs thereof. The membranes may be of cylindrical or planar  
5 geometry.

For shell and tube designs, the membrane comprises one or more tubular membranes each of which has an internal surface which defines an internal volume. In this aspect either the aqueous fluid or the acidic stripping solution is held within the internal volume of the  
10 tubular membrane(s) and the other of the aqueous fluid or the acidic stripping solution is in contact with the external surface of the tubular membrane(s). For spiral wound designs, either the aqueous fluid or the acidic stripping solution is within the membrane leaves and the other of the aqueous fluid or the acidic stripping solution is in contact with the external surface of the membrane leaves.

15

It will be appreciated that in an industrial setting preferably the aqueous fluid is held within the internal volume of the tubular membrane(s) and the acidic stripping solution is in contact with the external surface of the tubular membrane(s), and wherein the tubular membrane(s) and the acidic stripping solution are operably contained.

20

The membrane of the present invention is formed from or comprises a material suitable to provide a non-porous, selectively permeable membrane. The membrane may consist of a homogeneous membrane such as a tube or sheet of material, or a composite membrane. The composite membrane may comprise a non-porous, selectively permeable layer and  
25 one or more further materials or may comprise a mixture of materials. The non-porous, selectively permeable layer or material prevents direct contact of the aqueous stream with the acidic stripping solution. This is important. If a direct contact stripping device such as a packed or plate column or microporous membrane contactor is used, the two streams would mix and there would be no resulting separation.

30

In a preferred aspect the membrane or the non-porous, selectively permeable layer thereof

- is formed from or comprises a material selected from modified polysiloxane based elastomers including polydimethylsiloxane (PDMS) based elastomers, ethylene-propylene diene (EPDM) based elastomers, polynorbornene based elastomers, polyoctenamer based elastomers, polyurethane based elastomers, butadiene and nitrile butadiene rubber based elastomers, natural rubber, butyl rubber based elastomers, polychloroprene (Neoprene) based elastomers, epichlorohydrin elastomers, polyacrylate elastomers, polyethylene, polypropylene, polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF) based elastomers, and mixtures thereof.
- 10 In a preferred aspect the membrane comprises a reinforcing material selected from an external mesh and support. This is particularly advantageous for homogenous tubes or sheets. Such tubes or sheets may be reinforced to increase their burst pressure, for example by overbraiding tubes using fibres of metal or plastic, or by providing a supporting mesh for flat sheets.
- 15 When the membrane comprises a non-porous layer and an additional component, the additional component may be a supporting layer. The supporting layer may be a porous support layer. Suitable materials for the open porous support structure are well known to those skilled in the art of membrane processing. Preferably the porous support is formed from or comprises a material selected from polymeric material suitable for fabricating microfiltration, ultrafiltration, nanofiltration or reverse osmosis membranes, including polyethylene, polypropylene, polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF) polyethersulfone, and mixtures thereof.
- 20
- 25 Preferably the tubular membranes have a high length to diameter ratios for example the tubular membranes may have an internal diameters from 0.5 to 5.0 mm, and/or a wall thicknesses between 0.1 and 1.0 mm and/or a length of from 50 to 500 metres. The length to diameter ratio of the tubular membrane may be from  $1 \times 10^4$  to  $1 \times 10^6$ .
- 30 High length to diameter ratio such a those given above are considerably longer than the length to diameter ratios of membranes typically applied in prior art membrane extraction

processes, and have the advantage that the aqueous fluid entering the membrane tubes passes down a long flow path before emerging from the membrane. Thus it is possible to remove a high percentage of the aromatic amine contaminants in one pass down a single membrane tube, and this reduces the need for extensive manifolding which arises when the aqueous fluid must be passed through several or many membrane modules to achieve the desired degree of removal. This reduction in manifolding results in cost advantages over shorter membrane tubes.

In a further preferred aspect of the present invention a pH control system is used to regulate the flow of acidic stripping solution which contacts the membrane.

Control of pH in the acidic stripping solution is important. Upon contact with the membrane the acidic stripping solution pH will tend to be increased by the dissociation of the aromatic amine, and it is advantageous for the process efficiency that the pH of the acidic stripping solution is kept at least 0.5 pH units below the pKa of the aromatic amine. This may be achieved by fixing the flowrate and strength of the acidic stripping solution so as to ensure that this condition is always met. A higher acid concentration in the acidic stripping solution for given volumes or flows of aqueous fluid and acidic stripping solution will meet this condition better than a lower concentration of acid. A higher acid concentration also makes possible a lower acid flowrate for a given aromatic amine loading in the aqueous fluid; this results in a lower recycle stream flowrate from step (e), and hence a more cost effective system. However use of excessive acid in the acidic stripping solution will require excess alkali in the recovery stage. Also, excessively strong acids may damage the non-porous membrane. For example, silicone rubber is one of the most permeable elastomers and so desirable for use in the process, but can be damaged by acid concentrations above 1 wt.% mineral acid.

Preferably the stripping solution in contact with the nonporous membrane is well mixed so that its composition is well mixed throughout the volume operably in contact with the nonporous membrane.

Preferably the pH of the acidic stripping solution in contact with the non-porous membrane is controlled so that it is substantially the same throughout the acidic stripping solution in contact with the non-porous membrane separating layer.

5 Preferably the aqueous fluid contains an aromatic amine selected from aniline, chloroanilines, dichloroanilines, toluidines, dimethylaniline, nitroaniline, phenylaniline, methylaniline, ethylaniline, anisidine, benzylamine, fluoroanilines, difluoroanilines, aminophenols, and mixtures thereof.

10 Preferably the acidic stripping solution comprises a mineral acid selected from hydrochloric acid, sulphuric acid, phosphoric acid, nitric acid, and mixtures thereof.

Preferably the pH of the aromatic amine containing acidic stripping solution is adjusted in step (d) by the addition of an alkali.

15

Preferably the alkali is an aqueous solution of an alkali selected from sodium hydroxide, sodium carbonate, calcium hydroxide, calcium carbonate, potassium hydroxide, potassium carbonate, and mixtures thereof.

20 In a further preferred aspect the aqueous fluid is contacted with one side of a plurality of membranes in series, in parallel or in a combination thereof, and wherein the acidic stripping solution is contacted with the other side of each of the plurality of membranes.

The process may be performed in a continuous, semi-continuous or discontinuous (batch  
25 mode) manner. In the latter aspect the flow of at least one of the aqueous fluid, the acidic stripping solution, and the alkali solution is discontinuous.

In one aspect the resulting aromatic amine of step (e) is contacted with an organic solvent and subsequently treated in a further process. In this aspect it may be desirable to contact  
30 the amine containing acidic stripping solution and/or the separated aromatic amine with a solvent or solvent mixture in step (e). This may be particularly useful when the separated

aromatic amine is a solid. The solvent introduced may dissolve the solid. This may be further useful when this solid is a product or reactant in a reaction and where the solid and the solvent used to dissolve the solid can be sent to the further process in which the solid material is produced or consumed.

5

The process of the present invention may be performed in a reactor comprising at least a first zone, a second zone, a third zone, and a fourth zone; wherein each of the zones is discrete from each other zone; wherein the first zone and the second zone are separated by the non porous membrane; wherein the first zone contains the aqueous fluid ; wherein the  
10 second zone and fourth zone contain the acidic stripping solution; wherein the third zone contains amine containing acidic stripping solution; wherein the first zone and the third zone are operably connected to each other; wherein the second zone is operably connected to the third zone and the fourth zone; and wherein the acidic stripping solution is circulated between the fourth zone and the second zone such that the acidic stripping solution is well  
15 mixed throughout its volume.

Preferably, the acidic stripping solution is circulated between the fourth zone and the second zone at a high rate relative to the flow of aqueous fluid. By the term "high rate" it is preferably meant that the volume of acidic stripping solution contacted with the  
20 membrane is greater than the volume of aqueous fluid contacted with the membrane. The ratio of acidic stripping solution volume to aqueous fluid volume contacted with the membrane may be  $>2:1$ ,  $>5:1$ , or  $>10:1$ .

The aqueous fluid and/or the acidic stripping solution of the present invention may be  
25 heated before contact with the membrane. The aqueous fluid and/or the acidic stripping solution of the present invention may have a temperature above room temperature ( $25^{\circ}\text{C}$ ). This may increase the rate of mass transfer across the non-porous membrane.

In a further preferred aspect the aqueous fluid contains substantial quantities of dissolved  
30 inorganic or organic materials. By the term "substantial quantities" it is meant greater than 0.1 wt%. The inorganic materials may include salts, such as sodium chloride,

potassium chloride and mixtures thereof. The organic materials may include solvents, such as methanol, ethanol, acetone, acetate and mixtures thereof.

The aromatic amine in the acidic stripping solution dissociates according to an equilibrium reaction described by equation (1). Even at low pH, there will be some finite fraction of the aromatic amine present in dissociated form, and the total aromatic amine concentration will be equal to the sum of the concentration of dissociated and the concentration of undissociated aromatic amine. In general, the higher the concentration of total aromatic amine in the acidic stripping solution at a given pH, the higher will be the concentration of undissociated aromatic amine. This undissociated aromatic amine will act to reduce the driving force for mass transfer of undissociated aromatic amine from the aqueous fluid to the acidic stripping solution. This effect will be relatively greater for the aqueous fluid in the section of membrane near the point of exit of the aqueous fluid from the membrane.

Thus in a further preferred embodiment of the present invention, it is desirable to use two well mixed stripping stages in series. In this embodiment, the aqueous fluid first contacts a membrane whose other side is in contact with a well mixed strength 1 acidic stripping solution in a first stripping stage, and then contacts a second membrane whose other side is in contact with a well mixed strength 2 acidic stripping solution in a second stage. Strength of an acidic stripping solution is determined by the strength of the acid, for example, the mineral acid, fed to the acidic stripping solution. In this aspect, the mineral acid concentration fed to stripping solution 1 is stronger than the mineral acid concentration fed to stripping solution 2. The aqueous fluid passes from the membrane of stripping stage 1 to membrane of stripping stage 2. Mineral acid is fed to the acidic stripping solution in stripping stage 2, and the resulting strength 2 stripping solution from stage 2 is passed into stage 1 where further mineral acid is added to increase the strength of the acidic stripping solution in stage 1 to strength 1. The total aromatic amine concentration in stage 1 is greater than the total aromatic amine concentration in stage 2. The pH may be controlled to be constant in each stripping stage and may be set at different values in stage 1 and stage 2. The use of more than two stages is also envisaged.

The invention will now be described, by way of example only, with reference to the accompanying drawings, in which:-

- 5 Figure 1 is a schematic of an apparatus operating the process of the present invention.  
Figure 2 is a schematic of an apparatus operating the process of the present invention.  
Figure 3 is a schematic of an apparatus operating the process of the present invention.  
Figure 4 is a schematic of an apparatus operating the process of the present invention.  
Figure 5 is a schematic of an apparatus operating the process of the present invention.  
10 Figure 6 is a schematic of an apparatus operating the process of the present invention.

Figure 1 shows a schematic of one embodiment of the process. The aqueous fluid containing undissociated aromatic amines (1) passes on one surface of a membrane containing at least one non-porous separating layer (5), optionally mounted in a  
15 membrane module (6). Undissociated aromatic amines in the wastewater permeate across the membrane into the acidic stripping solution (3), whose pH is such that the aromatic amines are converted into their corresponding salts. The aqueous fluid exiting the membrane has a reduced concentration of aromatic amines relative to the aqueous fluid (1) entering the membrane. The aromatic amine laden acidic stripping solution (4) leaves  
20 the membrane module (6) containing dissociated aromatic amines and enters a neutralisation vessel (7). By manipulation of the ratio between the volume of aqueous stream fed (1) and volume of acidic stripping solution fed (3), i.e. by using a ratio greater than 1, the concentration of dissociated aromatic amines in aromatic amine laden acidic stripping solution (4) is elevated to levels higher than the saturation concentration of  
25 undissociated aromatic amines in water. In the neutralisation vessel (7) a mineral alkali (8) is added to adjust pH of the solution to a value above the pKa of the aromatic amine. This converts the aromatic amine back to an undissociated form. Since it is at a concentration higher than the saturation concentration of undissociated amine in water, the aromatic amine precipitates out of solution as a liquid or solid. The neutralisation  
30 vessel (7) may be optionally stirred. The resulting two phase mixture (9) is passed to a settling vessel (10) where the two phases are separated. The organic phase (either liquid

or solid) is removed (11) from the settling vessel (10), and the aromatic amine saturated aqueous layer (12) is recirculated back either to the aqueous process stream (1), or to the neutralisation tank (7).

- 5 In a preferred embodiment, the membranes may comprise a bundle of tubular membranes with suitable head piece connections for allowing flow of the aqueous fluid to pass through the interior of the membranes. This bundle of tubular membranes may be suspended in a tank or other vessel so that the outside surface of the fibres is substantially immersed in the acidic stripping solution. In this case the acidic stripping solution will be  
10 mixed or agitated using a stirrer or pump or some other suitable device to ensure that the acidic stripping solution is well mixed at all times and the composition of the stripping solution in contact with the membrane will be the same as the concentration of the stripping solution (4) leaving the tank (15). Figure 2 shows this general arrangement where a bundle of tubular membranes (13) are connected at each end to allow wastewater  
15 flow through headpieces (14), and are immersed in a tank (15) of acidic stripping solution.

- Figure 3 shows yet another preferred embodiment, in which one or more elastomeric tubular membranes (16) connected using suitable headpieces (17) are suspended in a well mixed tank (15) containing acidic stripping solution (4). The elastomeric tubular  
20 membranes can be coiled, stacked or otherwise arranged in the tank so that they have their surfaces substantially immersed in the acidic stripping solution (4). It is advantageous in this embodiment to use elastomeric tubular membranes which have high length to diameter ratios for example the elastomeric tubular membranes might have internal diameters from 0.5 to 5.0 mm, wall thicknesses between 0.1 and 1.0 mm and lengths from  
25 50 to 500 metres, i.e. length to diameter ratios of  $1 \times 10^4$  to  $1 \times 10^6$ .

- The configurations illustrated in Figures 2 and 3 are made possible by the rapid dissociation reaction in the acidic stripping solution which removes the need to configure the flow over the outside surfaces of the membrane so as to provide high rates of film  
30 mass transfer.



It is apparent to one skilled in the art that it is desirable to use a strong acid (by way of non limiting example, hydrochloric acid above 20 wt.% (HCl), as a feed acidic stripping solution (3), while maintaining pH in the acidic stripping solution in contact with the non-porous membrane (4) separating layer at a high enough value to minimise the need for alkali addition and to ensure maximal lifetime of the non-porous membrane separating layer. It is with these objectives in mind that the configurations of Figures 2, 3, 4 and 5 are found to have advantages over passing the aqueous and organic streams in countercurrent flow through membrane modules as shown in Figure 1. In the configurations of Figures 2, 3, 4 and 5 the acid added (3) can be concentrated but as it is immediately mixed into the aromatic amine laden acidic stripping solution (4) in the well mixed tank (15) the actual acid concentration of the acidic stripping solution in contact with the non-porous membrane separating layers can be everywhere substantially less than the acid concentration of the feed acidic stripping solution (3).

A further preferred embodiment of the process as shown in Figure 4 by way of non-limiting example can be employed. A well mixed tank (15) containing an elastomeric membrane tube (16) immersed in acidic stripping solution (4) has a pH sensor (18) in contact with the well mixed acidic stripping solution (4). This pH sensor measures pH and transmits this information to a control device (19) which regulates flow of feed acidic stripping solution (3) to the tank to hold pH at the desired value. Using this approach pH in the tank (15) can be controlled to the highest value consistent with good process efficiency, thus minimising acidity in the tank and in the aromatic amine laden acidic stripping solution (4). This has consequent advantages for neutralisation costs and membrane lifetime.

25

In yet another preferred embodiment, shown in Figure 5, the advantages of a well mixed acidic stripping solution in a remote stripping tank (20) are shown in connection with the use of a membrane module of the type used in Figure 1. The pH is controlled in the stripping tank by a pH sensor (18) and a control device (19) which regulates the flow feed acidic stripping solution (3) to the stripping tank (20). The acidic stripping solution is recirculated (21) to the membrane module or modules at a high rate so that for all

30

practical purposes the acidic stripping solution can be considered well mixed throughout its volume. Aromatic amine laden acidic stripping solution is withdrawn (4) and passed to the neutralisation tank (7).

- 5 In yet another preferred embodiment the temperature of the acidic stripping solution in tank (15) or tank (20) and or the aqueous stream (1) can be increased above ambient conditions to increase the rate of mass transfer across the non-porous separating layer of the membrane.
- 10 In yet another preferred embodiment shown in Figure 6, the use of two stripping stages is shown with two strengths of acidic stripping solution. The aqueous fluid (1) enters the first stripping stage in which a membrane (30) is suspended in the first stage tank (31). An acidic stripping solution containing mineral acid (32) is added to the stage 1 tank (31) automatically by a pH controller (34) connected to a pH probe (33). The stripping solution
- 15 in stage 1 is well mixed throughout the volume of the stage 1 tank (31) so that it is of identical composition to the stripping solution (42) exiting the stage 1 tank. The aqueous fluid (35) flows out of stage 1 and into stage 2 where a second membrane (40) is suspended in the stage 2 tank (41). The aqueous fluid (2) flows out of the second membrane (40) with a reduced concentration of aromatic amine relative to stream (1). In
- 20 the second stage, acidic stripping solution containing mineral acid (37) at a lower concentration than stream (32) is added to the stage 2 tank (41) automatically by a pH controller (39) connected to a pH probe (38). The stripping solution in the stage 2 tank (41) is well mixed throughout the volume of the stage 2 tank so that it is of identical composition to the stripping solution (36) exiting the stage 2 tank. The stripping solution
- 25 (36) exiting the stage 2 tank (41) is fed to the stage 1 tank (31). The system is configured and operated so that the total aromatic amine concentration in stream (36) is less than the total aromatic amine concentration in stream (42). The stripping solution (42) from the stage (1) tank is passed to the neutralisation vessel (7). Following phase separation, the aromatic amine saturated aqueous layer (12) is recirculated back to the aqueous fluid (1).

30

The processes described above may be operated continuously, semi-continuously or in

batch mode. The tanks may be single tanks or multiples tanks. The neutralisation vessel (7) and the phase separating vessel (10) may be combined into the same vessel. Mixing of one or all of the tanks may be achieved by using any device known to those skilled in the art, such as mixers, pumps, or air lift devices. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

The invention will now be described in further detail in the following non-limiting Examples.

## 10 EXAMPLES

### EXAMPLE 1

The following example describes batch operation of the present invention. 1000 mL of acidic stripping solution comprising a dilute solution of hydrochloric acid were added to a stirred tank containing a 13 metre length of a silicone rubber membrane tube with internal diameter of 3 mm, wall thickness 0.6 mm. 20 litres of a wastewater containing 0.6 wt.% aniline were recirculated from a drum through the inside of the elastomeric membrane tube. Concentrated (37 wt.%) hydrochloric acid was added regularly to the acidic stripping solution to maintain pH in the range 1-4. After 14 days the experiment was stopped, and the acidic stripping solution removed. The pH of the acidic stripping solution was adjusted to 11 by addition of 40 wt.% NaOH solution, and a dark organic liquid formed and was separated. This organic liquid was analysed via gas chromatography and found to be more than 99% pure aniline.

### EXAMPLE 2

The following example describes continuous operation of the present invention. 1000 mL of acidic stripping solution were added to a stirred tank containing a 10 metre length of a silicone rubber membrane tube with internal diameter of 3 mm, wall thickness 0.6 mm. A pH sensor was suspended in the tank and a controller was connected to the sensor so as to

add 37 wt.% hydrochloric acid to the tank when required to maintain pH. The controller held pH at 2.5 +/- 0.2 pH units. A flow of aqueous process stream containing aniline at 0.5 wt.% was pumped from a drum and passed through the inside of the membrane tube. The overflow of the acidic stripping solution was periodically removed to a tank where  
5 pH was adjusted, resulting in formation of a dark organic liquid. The resulting aqueous and organic phases were separated and the aqueous phase mixed with the aqueous process stream in the drum. The dark organic liquid was analysed and found to be aniline.

### EXAMPLE 3

10

The following example describes batch operation of the present invention used to recover 2,4 difluoroaniline from an aqueous stream. 1000mL of strip solution comprising a dilute solution of hydrochloric acid were added to a stirred tank containing a 50 metre length of a silicone rubber membrane tube with internal diameter of 3mm, wall thickness 0.6 mm.  
15 20 litres of a wastewater containing 0.35wt% 2,4 difluoroaniline were recirculated from a drum through the inside of the elastomeric membrane tube. Concentrated (37wt%) hydrochloric acid was added regularly to the strip solution to maintain pH in the range 1.5-2.0. After 4 days the experiment was stopped, and the strip solution removed. The pH  
of the strip solution was adjusted to 11 by addition of 40wt% NaOH solution, and a dark  
20 organic liquid formed and was separated. This organic liquid was analysed via gas chromatography and found to be more than 99% pure 2,4 difluoroaniline.

### EXAMPLE 4

25 The following example describes batch operation of the process to recover a mixture of 2,4 difluoroaniline and 2,4,6 bromodifluoroaniline from an aqueous waste. 1000mL of strip solution comprising a 10%wt solution of hydrochloric acid were added to a stirred tank containing a 20 metre length of an EPDM rubber membrane tube with internal diameter of 3mm, wall thickness 1 mm. 20 litres of a wastewater containing 0.35wt% 2,4  
30 difluoroaniline and 0.15 wt% 2,4,6 bromodifluoroaniline were recirculated from a drum through the inside of the elastomeric membrane tube. After 4 days the experiment was

stopped, and the strip solution removed. The pH of the strip solution was adjusted to 11 by addition of 40wt% NaOH solution, and a dark organic liquid formed and was separated. This organic liquid was analysed via gas chromatography and found to be more than 20% 2,4 difluoroaniline and 80% 2,4,6 bromodifluoroaniline.

5

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with  
10 specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the  
15 following claims.

## CLAIMS

1. A process for removing and recovering one or more undissociated aromatic amines dissolved in aqueous fluid, the process comprising the steps of:
  - 5 (a) transferring the one or more undissociated aromatic amines from the aqueous fluid to an acidic stripping solution, wherein transfer of the one or more undissociated aromatic amines from the aqueous fluid to the acidic stripping solution occurs across a membrane; wherein the membrane is a non porous, selectively permeable membrane;
  - (b) regulating the volume of acidic stripping solution employed relative to the volume of  
10 aqueous fluid treated so that the total aromatic amine concentration in the acidic stripping solution, comprising the sum of the dissociated and undissociated aromatic amine concentrations, is above the solubility of the aromatic amines in water;
  - (c) regulating the pH of the acidic stripping solution in contact with the membrane so that the membrane remains selectively permeable;
  - 15 (d) adjusting the pH of the aromatic amine containing acidic stripping solution to a value above the acidic dissociation constant of the aromatic amine and
  - (e) separating the resulting aromatic amine and the acidic stripping solution.
2. A process according to claim 1 wherein the aqueous fluid is an aqueous process  
20 stream.
3. A process according to claim 1 or 2 wherein the aqueous fluid is contacted with one side of the membrane and wherein the acidic stripping solution is contacted with the other side of the membrane.  
25
4. A process according to claim 3 wherein prior to adjusting the pH of the aromatic amine containing acidic stripping solution, the acidic stripping solution is removed from contact with the membrane.
- 30 5. A process according to claim 3 or 4 wherein the acidic stripping solution separated in step (e) is recycled to the aqueous fluid prior to contact with the membrane.

6. A process according to claim 4 wherein the acidic stripping solution separated in step (e) is recycled to the aromatic amine containing acidic stripping solution prior to removing the acidic stripping solution from contact with the membrane.

5

7. A process according to any one of the preceding claims wherein the resulting aromatic amine of step (e) is a liquid.

8. A process according to any one of claims 1 to 6 wherein the resulting aromatic  
10 amine of step (e) is a solid.

9. A process according to any one of the preceding claims wherein the membrane is mounted in a plate and frame configuration, a shell and tube configuration, or a spiral wound configuration.

15

10. A process according to any one of the preceding claims wherein the membrane comprises one or more tubular membranes each of which has an internal surface which defines an internal volume and either the aqueous fluid or the acidic stripping solution is held within the internal volume of the tubular membrane(s) and the other of the aqueous  
20 fluid or the acidic stripping solution is in contact with the external surface of the tubular membrane(s).

11. A process according to claim 10 wherein the aqueous fluid is held within the internal volume of the tubular membrane(s) and the acidic stripping solution is in contact  
25 with the external surface of the tubular membrane(s), and wherein the tubular membrane(s) and the acidic stripping solution are operably contained.

12. A process according to claim 10 or 11 wherein the tubular membrane(s) is elastomeric.

30

13. A process according to any one of claims 10 to 12 wherein the tubular

membrane(s) has a length to diameter ratio of from 10,000 to 1,000,000.

14. A process according to any one of the preceding claims wherein the acidic stripping solution in contact with the nonporous membrane is well mixed throughout its  
5 volume such that its composition is uniform throughout.

15. A process according to any one of the preceding claims wherein the pH of the acidic stripping solution in contact with the non-porous membrane is controlled so that it is substantially the same throughout the volume of acidic stripping solution in contact  
10 with the non-porous membrane separating layer.

16. A process according to any one of the preceding claims wherein the aqueous fluid contains an aromatic amine selected from aniline, chloroanilines, dichloroanilines, toluidines, dimethylaniline, nitroaniline, phenylaniline, methylaniline, ethylaniline,  
15 anisidine, benzylamine, fluoroanilines, difluoroanilines, aminophenols and mixtures thereof.

17. A process according to any one of the preceding claims wherein the acidic stripping solution comprises a mineral acid selected from hydrochloric acid, sulphuric  
20 acid, phosphoric acid, nitric acid, and mixtures thereof.

18. A process according to any one of the preceding claims wherein the pH of the aromatic amine containing acidic stripping solution is adjusted in step (d) by the addition of an alkali.  
25

19. A process according to claim 18 wherein the alkali is an aqueous solution of an alkali selected from sodium hydroxide, sodium carbonate, calcium hydroxide, calcium carbonate, potassium hydroxide, potassium carbonate, and mixtures thereof.

30 20. A process according to any one of the preceding claims wherein the membrane is formed from or comprises a material selected from modified polysiloxane based



elastomers, ethylene-propylene diene (EPDM) based elastomers, polynorbornene based elastomers, polyoctenamer based elastomers, polyurethane based elastomers, butadiene and nitrile butadiene rubber based elastomers, natural rubber, butyl rubber based elastomers, polychloroprene (Neoprene) based elastomers, epichlorohydrin elastomers, polyacrylate elastomers, polyethylene, polypropylene, polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF) based elastomers, and mixtures thereof.

21. A process according to claim 20 wherein the modified polysiloxane based elastomer is a polydimethylsiloxane (PDMS) based elastomer.

22. A process according to any one of the preceding claims wherein the membrane comprises a reinforcing material selected from an external mesh and support.

23. A process according to any one of the preceding claims wherein the membrane is a composite membrane comprising a porous support and at least one non-porous layer.

24. A process according to claim 23 where the porous support is formed from or comprises a material selected from polymeric material suitable for fabricating microfiltration, ultrafiltration, nanofiltration or reverse osmosis membranes, including polyethylene, polypropylene, polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF) polyethersulfone, and mixtures thereof.

25. A process according to any one of the preceding claims wherein the aqueous fluid is contacted with one side of a plurality of membranes in series, in parallel or in a combination thereof, and wherein the acidic stripping solution is contacted with the other side of each of the plurality of membranes.

26. A process according to any one of the preceding claims wherein the process is performed in a continuous manner.

27. A process according to any one of claims 19 to 25 wherein the flow of at least one

of the aqueous fluid, the acidic stripping solution, and the alkali solution is discontinuous.

28. A process according to any one of the preceding claims wherein the resulting aromatic amine of step (e) is contacted with an organic solvent and subsequently treated  
5 in a further process.

29. A process according to any one of the preceding claims wherein the process is performed in a reactor comprising at least a first zone, a second zone, a third zone, and a fourth zone

10 wherein each of the zones is discrete from each other zone;  
wherein the first zone and the second zone are separated by the non porous membrane;  
wherein the first zone contains the aqueous fluid ;  
wherein the second zone and fourth zone contain the acidic stripping solution;  
wherein the third zone contains amine containing acidic stripping solution;  
15 wherein the first zone and the third zone are operably connected to each other;  
wherein the second zone is operably connected to the third zone and the fourth zone;  
and wherein the acidic stripping solution is circulated between the fourth zone and the second zone such that the acidic stripping solution is well mixed throughout its volume.

20 30. A process according to claim 29 wherein a pH control system is used to regulate the flow of acidic stripping solution between the fourth zone and the second zone.

31. A process according to any one of the preceding claims wherein at least one of the aqueous fluid and the acidic stripping solution has a temperature above room temperature.

25

32. A process according to any one of the preceding claims wherein the aqueous fluid contains substantial quantities of dissolved inorganic or organic materials.

33. A process as substantially described herein and with reference to any one of  
30 Figures 1-6.

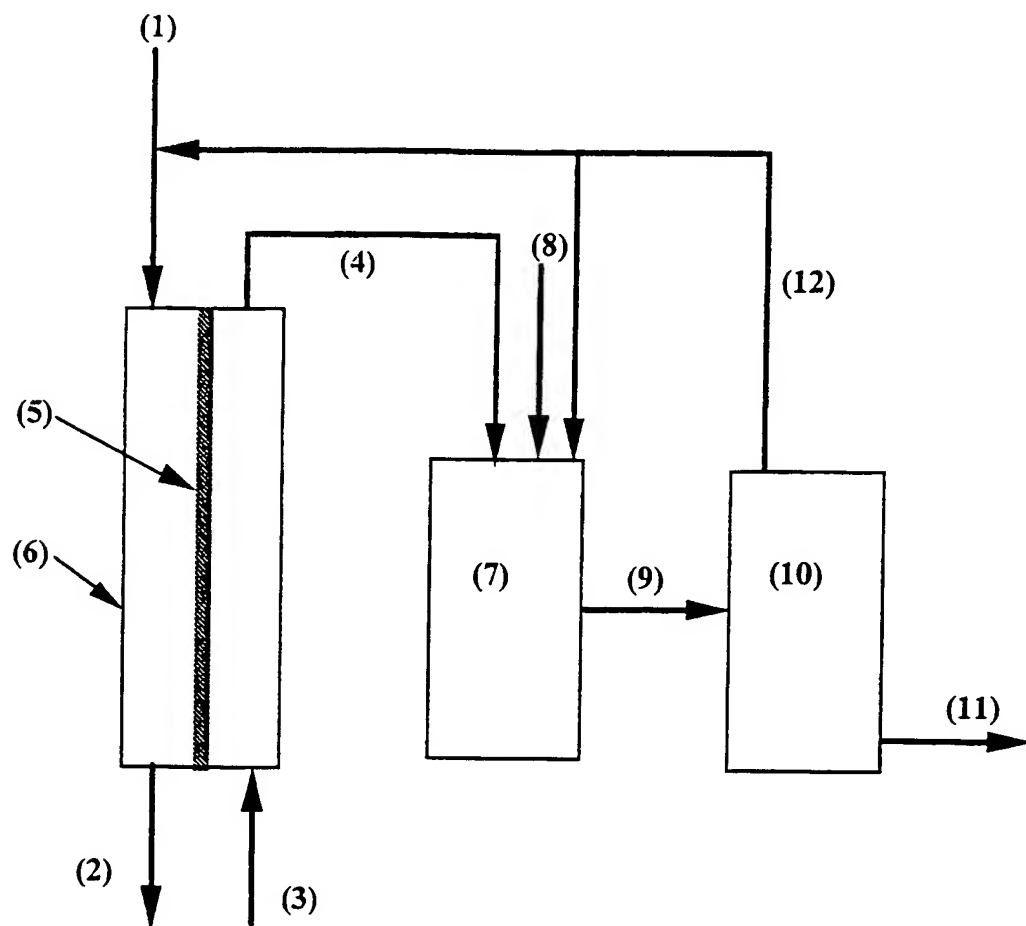
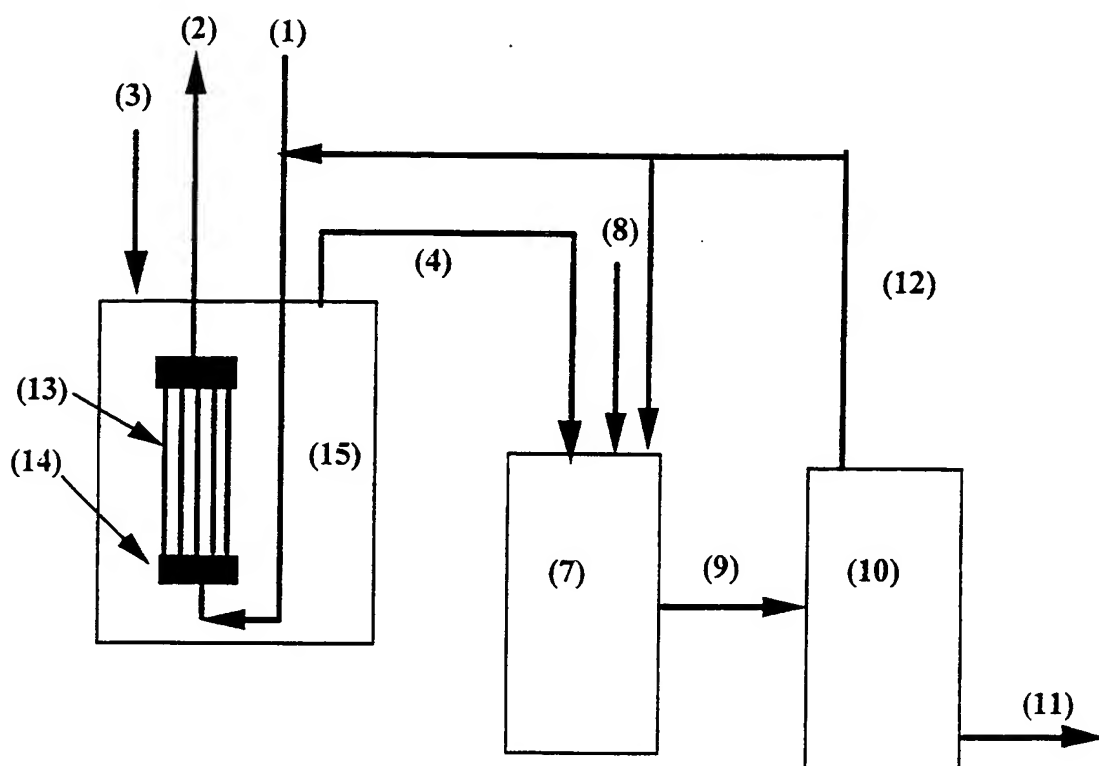


Figure 1 - Aromatic amine recovery process

2/6



**Figure 2- Aromatic amine recovery process with bundle of tubular membranes**

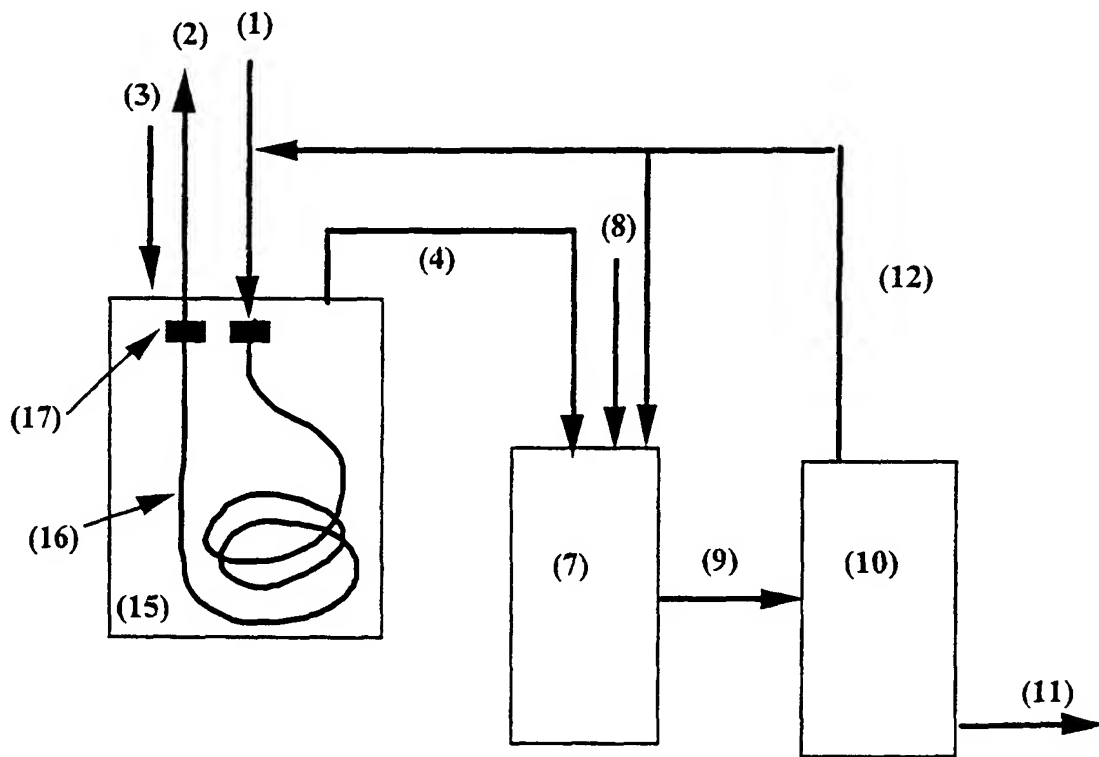


Figure 3- Aromatic amine recovery process with elastomeric tube membrane

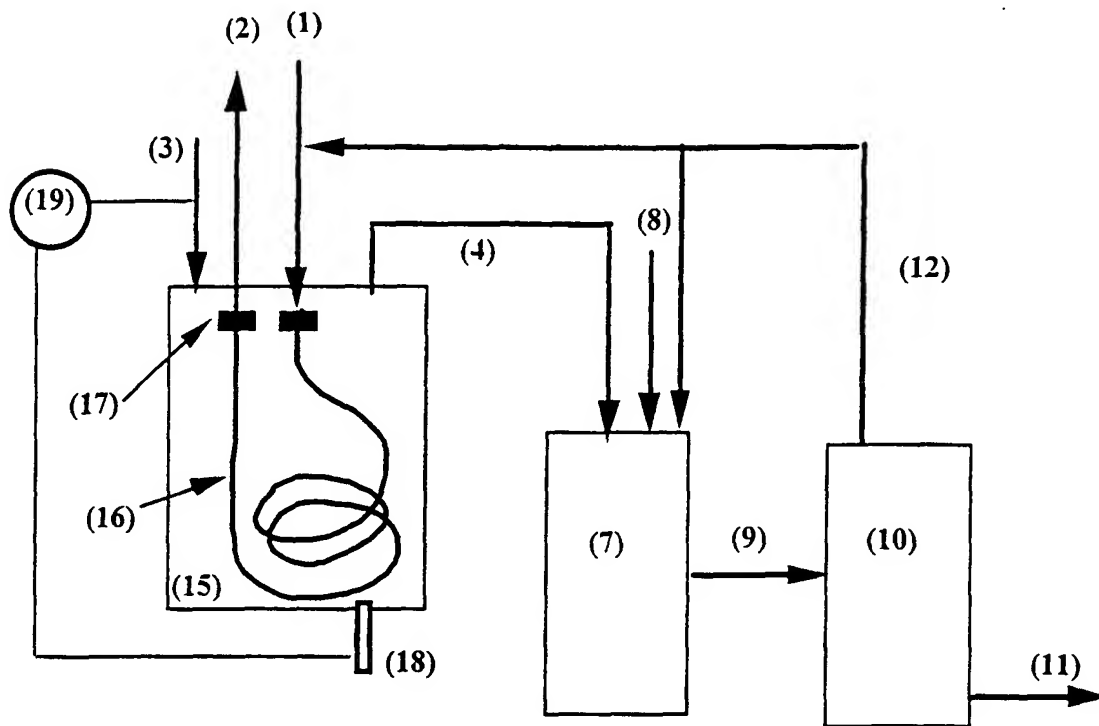
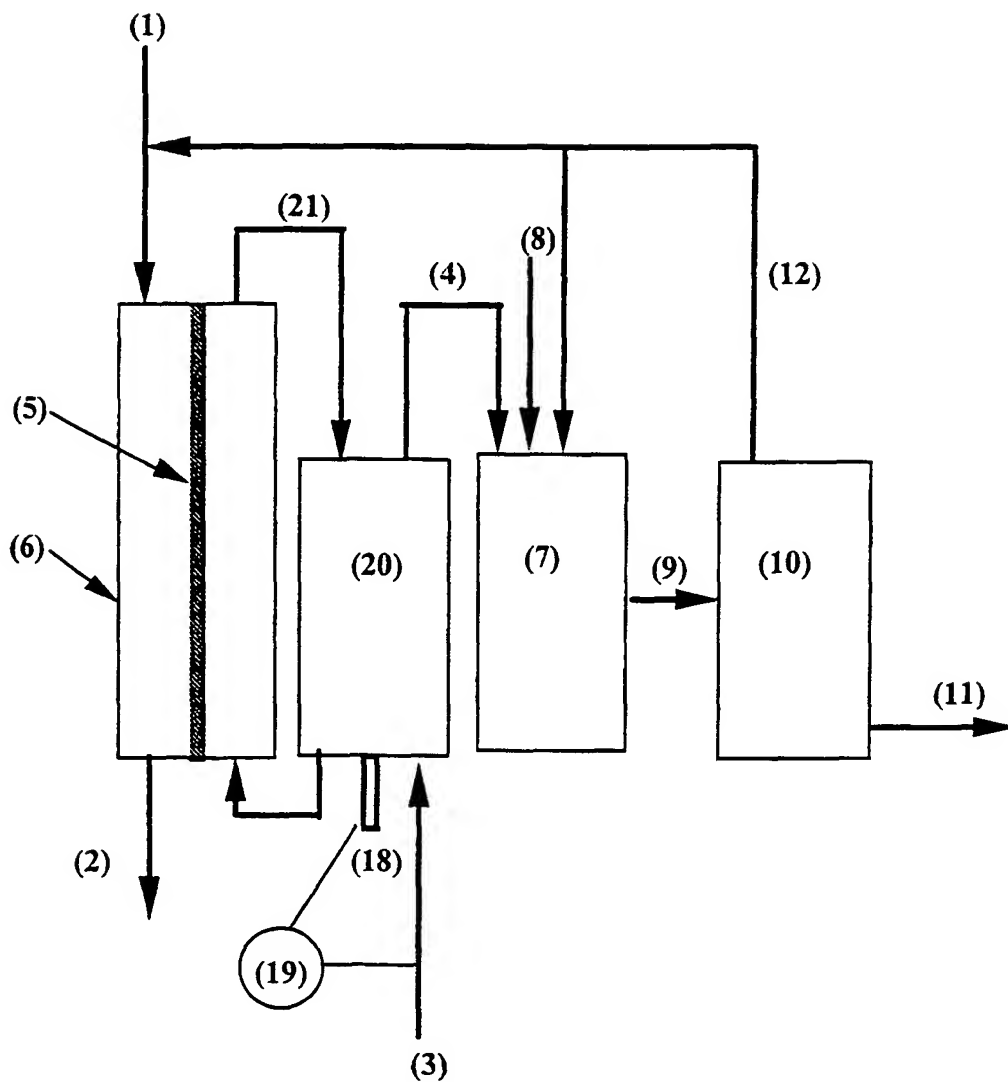


Figure 4- aromatic amine recovery process with elastomeric tube membrane and pH control



**Figure 5 - Aromatic amine recovery process operated with a well mixed stripping solution recirculated at high rate to a remote membrane module.**

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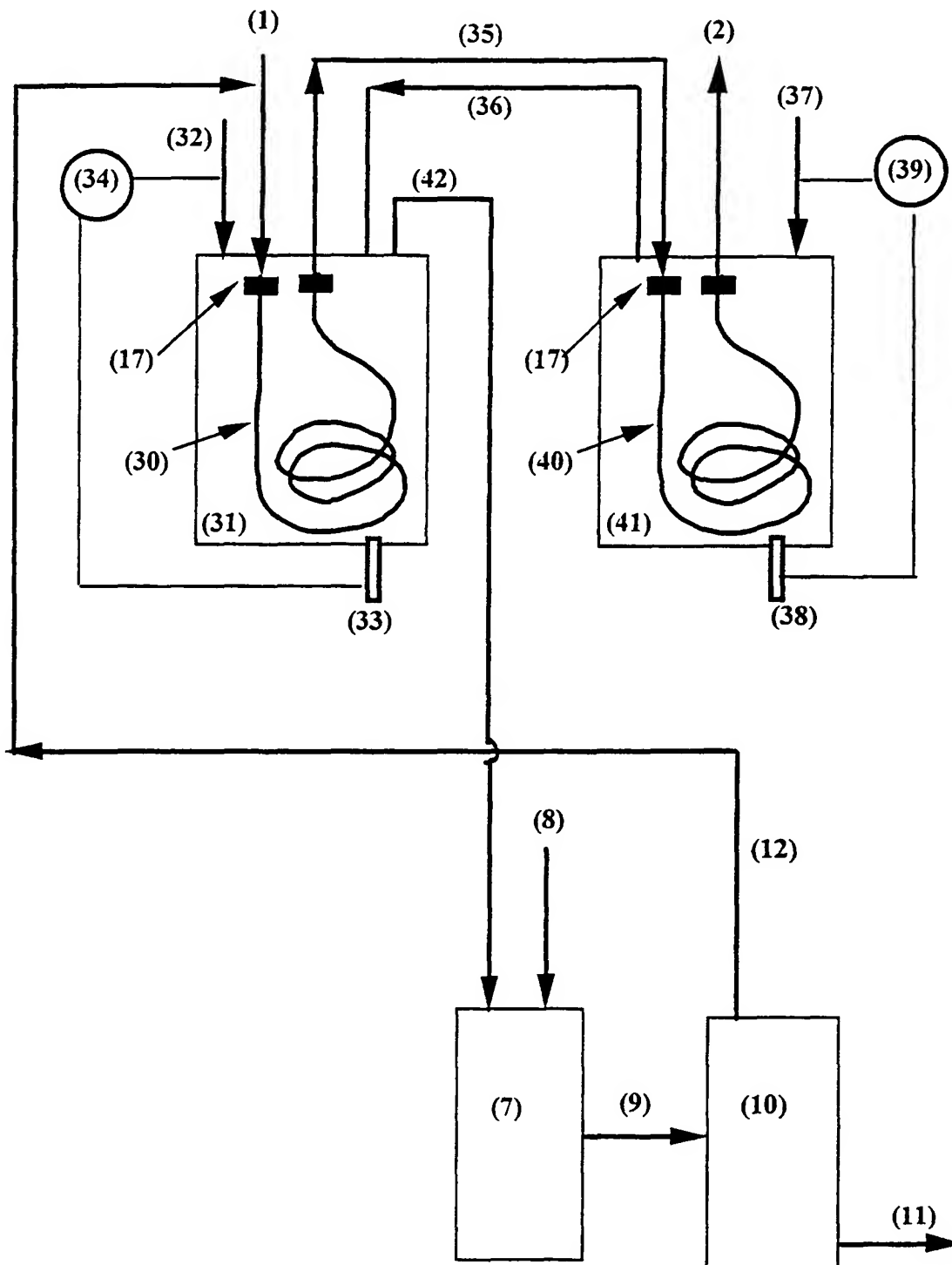


Figure 6 - Two stage aromatic amine recovery process



## INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/GB 00/02827

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/44 B01D61/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 333 473 A (MEMBRANE EXTRACTION TECHNOLOGY) 28 July 1999 (1999-07-28) page 6, line 6 -page 8, line 30 ----	1-32
A	US 5 585 004 A (LIVINGSTON ANDREW) 17 December 1996 (1996-12-17) cited in the application column 2, line 6 -column 4, line 54 ----	1-32
P,A	WO 00 00275 A (LIVINGSTON ANDREW GUY ;MEMBRANE EXTRACTION TECHNOLOGY (GB)) 6 January 2000 (2000-01-06) ----	
A	EP 0 485 077 A (EXXON RESEARCH ENGINEERING CO) 13 May 1992 (1992-05-13) -----	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the international search

1 December 2000

Date of mailing of the international search report

19/12/2000

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Interr. Application No.

PCT/GB 00/02827

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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US 5585004	A	17-12-1996	AT 189669 T AU 670041 B AU 2588592 A CA 2119383 A DE 69230667 D DE 69230667 T EP 0604514 A WO 9306045 A JP 6510696 T	15-02-2000 04-07-1996 27-04-1993 01-04-1993 16-03-2000 31-08-2000 06-07-1994 01-04-1993 01-12-1994
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EP 0485077	A	13-05-1992	US 5234597 A CA 2054046 A JP 4266989 A US 5435918 A	10-08-1993 06-05-1992 22-09-1992 25-07-1995

## P A T E N T COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
 US Department of Commerce  
 United States Patent and Trademark  
 Office, PCT  
 2011 South Clark Place Room  
 CP2/5C24  
 Arlington, VA 22202  
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 in its capacity as elected Office

Date of mailing (day/month/year) 25 June 2001 (25.06.01)	
International application No. PCT/GB00/02827	Applicant's or agent's file reference P7259WO DAA
International filing date (day/month/year) 21 July 2000 (21.07.00)	Priority date (day/month/year) 30 July 1999 (30.07.99)
Applicant LIVINGSTON, Andrew, Guy	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
 23 January 2001 (23.01.01)

☐ in a notice effecting later election filed with the International Bureau on:  
 \_\_\_\_\_

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Zakaria EL KHODARY
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38